# Computational Simulation on Electrowinning for Used LiCl-KCl salts

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## 1. Introduction

Pyrochemical processing has been developed as a important technology to recycle useful resources and separate long living radioactive elements from spent nuclear fuel. Used salt purification process which liquid metal and metal chloride are used in has been developed to prevent more actinides from being disposed of final vitrified waste. That purification is consisted of electrowinning with liquid metal cathode and selective oxidation with chemical equilibrium by using metal chloride as an oxidizing agent. Actinides and rare earth elements are deposited to liquid cathode in electrowinning and rare earth elements are selectively extracted to molten salt, however, codeposited Li react to oxidizing agent prior to rare earth elements which are intended to react in selective oxidation. Also if termination point of actinides deposition in electrowinning is clearly known, we would decrease amount of reacting rare earth elements as well as Li and throughput could be enhanced.

For pyroprocess research computational simulation is important to save limited resources and research environment. This study shows computational modeling on electrowinning with Bi cathode by using electrochemical simulation code REFIN.

## 2. Methods and Results

### *2.1 Computational Model Description*

REFIN, one-dimensional time-dependent simulation code, was developed by Seoul National University to analyze electrochemical process based on first principle [1]. REFIN can calculate various properties such as current densities, potential distributions for each element based on multi-species electrolysis especially with molten salt. Also it is simulated that surface concentration and the amount of materials which are dissolved or deposited as a function of time. REFIN calculate single electrochemical reactions on electrode by solving Butler-Volmer equation as represented in Eq 1 and mass transport in diffusion layer by solving diffusion and electromigration as represented in Eq 2. The code was verified by using experimental data collected by Tomczuk et al. and results from MARK-IV electrorefiner [1, 2].

$$i_j = i_{0,j}\left[\exp\left(\frac{\alpha_j n_j F}{RT}\eta_j\right) - \exp\left(-\frac{\left(1-\alpha_j\right)n_j F}{RT}\eta_j\right)\right] \quad (1)$$

$$\mathbf{J}_i = -D_i\Gamma_i\nabla C_i - \frac{F}{RT}z_i D_i C_i \nabla\Phi + C_i\mathbf{v}_i \quad (2)$$

### *2.2 Modeling Condition*

REFIN needs standard electrode potential, diffusion coefficient in both molten salt and liquid cathode, exchange current density, transfer coefficient and salt composition of each element to calculate electrochemical reaction. Table 1 shows those input parameters for REFIN simulation. Concentration means weight ratio for chloride of each element.

Table 1: Properties of elements included in used molten salt

| | Np | Pu | Am | La | Ce | Pr | Nd |
|---|---|---|---|---|---|---|---|
| Concentration [wt.%] | 0.006 | 0.099 | 0.005 | 1.092 | 2.129 | 1.000 | 3.621 |
| Standard electrode potential [V vs. $Cl_2$/Cl-] | -2.697 | -2.803 | -2.865 | -2.974 | -3.044 | -2.992 | -2.944 |
| Diffusion coefficient in molten salt | 1.703E-5 | 1.703E-5 | 1.703E-5 | 1.611E-5 | 1.611E-5 | 1.611E-5 | 1.611E-5 |
| Diffusion coefficient in liquid bismuth | 2.696E-5 | 2.696E-5 | 2.696E-5 | 2.550E-5 | 2.550E-5 | 2.550E-5 | 2.550E-5 |
| Exchange current density (Assumed) | 1.0E-6 | 1.0E-6 | 1.0E-6 | 1.0E-6 | 1.0E-6 | 1.0E-6 | 1.0E-6 |
| Transfer coefficient (Assumed) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |

In order to determine element and salt composition for modeling, it is assumed that the pyroprocessing flowsheet of KAERI as represented in report of OECD [3]. We consider used salt from electrorefining and

electrowinning for U recovery and TRU recovery, respectively. The ratio of TRU elements and RE elements are calculated by ORIGEN2.1 as assuming 4.5% of burn-up on $UO_2$ fuel and 5 years cooling after release from PWR. There are more than 15 elements for considering all of TRU and RE element in spent nuclear fuel, however, 7 major elements such as Np, Pu, Am and La, Ce, Pr, Nd are assumed to represent TRU and RE for computational efficiency. Those 7 elements are determined in the order of mass concentration of each group by ORIGEN2.1 calculation. Standard electrode potential is derived by Gibbs free energy [4]. Diffusion coefficient is calculated by Stokes-Einstein equation. Exchange current density and transfer coefficient are assumed with same values. Diffusion boundary layer thickness is assumed as 2.0E-3 cm. Applied current density is 10 mA/cm$^2$.

### *2.3 Simulation Results*

Fig. 1 and Fig. 2 show concentration change of each element in molten salt and liquid cathode which is caused by electrodeposition according to time.

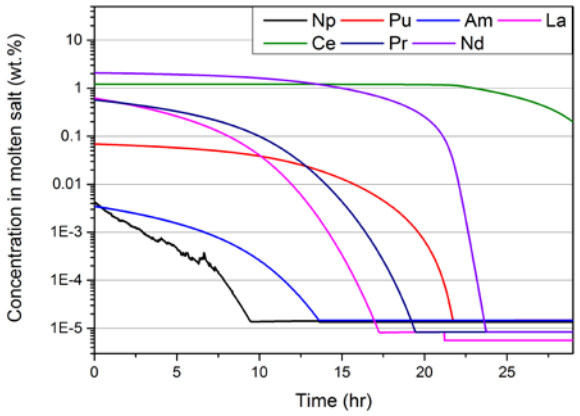


Fig. 1. Concentration change in molten salt.

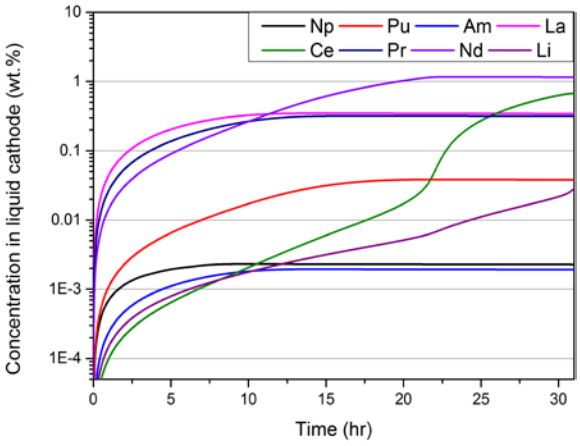


Fig. 2. Concentration change in liquid cathode.

Those figures indicate Np and Am which are relatively noble are depleted in molten salt phase and deposited to cathode. Pu is noble rather than RE elements but Pu takes possess huge amount compare with other TRU elements so the behavior is similar with RE elements. Likewise, deposition behavior of La and Pr is similar and faster than Ce and Nd which exist a lot in molten salt. Lithium is slowly reduced to cathode until Pu is depleted in molten salt. After that Li is rapidly reduced. It indicates that point could be considered to termination for electrowinning process in terms of salt purification by preventing electrodeposit from being contaminated by large amount of Li as well as Ce and Nd.

## 3. Conclusions

Computational simulation on electrowinning is investigated by using verified code, REFIN. This study shows that it is possible to simulate electrochemical behaviors of at least seven elements (excluding electrode and electrolyte materials) according to real time. In order to enhance accuracy of simulation results, it is suggested that combination of REFIN and CFD modeling on two immiscible liquid to calculate diffusion boundary layer thickness as well. Also it is necessary to more accurate properties such as diffusion coefficient, exchange current density and transfer coefficient which are assumed in this study.

## Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science, ICT and Future Planning, Republic of Korea (MSIP). (NRF-2011-0031839, NRF-2011-0031890)

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